*J. Phys. Chem. A* **2002,** *106,* 267−271

# Intracluster Reactions of $(CS_2)_n^-$ and $(OCS)_n^-$ Induced by Surface Impact

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*Received: July 5, 2001; In Final Form: September 21, 2001*

We investigated an intracluster reaction induced by impact of $(CS_2)_n^-$ ($n = 1-8$) onto silicon and $(La_{0.7}Ce_{0.3})B_6$ surfaces at collision energies of 100−2000 eV and 0−100 eV, respectively. Product anions scattered from the surfaces were mass analyzed by a tandem time-of-flight (TOF) mass spectrometer. In the impact onto the silicon surface, the intracluster reaction proceeds via (1) production of $S^-$ by dissociation of the core ion, $CS_2^-$, and (2) production of $S_m^-$ ($m = 2,3$) by abstractions of S from surrounding $CS_2$ by $S_{m-1}^-$. In the impact onto a $(La_{0.7}Ce_{0.3})B_6$ surface, essentially the same reaction mechanism operates except for the dimer reaction at collision energies less than 50 eV. The two isomers, $CS_2^-(CS_2)$ and $C_2S_4^-$, give $S_2^-$, and the latter dissociates further into $C_2S_2^-$. A similar reaction mechanism is found to operate in the intracluster reaction of $(OCS)_n^-$.

## Introduction

When a "soft" cluster is allowed to collide onto a hard surface, the cluster is deformed so rapidly that its constituent particles (atoms, molecules, etc.) are impacted on the surface instantaneously at the collision. As a result, the internal energy and the particle density of the cluster increase greatly in a very short period of time.[1−43] Evidently, this effect is more pronounced in the impact of a larger cluster onto a solid surface. It is expected, under such a non-equilibrium condition, that novel reactions, which are scarcely encountered in conventional reaction media, are likely to proceed by the cluster-impact (defined as "cluster-impact reaction").

It seems that there are two important factors to characterize the cluster-impact reaction; multiple collisions and short interatomic distances between the constituent particles. Levine and co-workers have predicted computationally that a four-center reaction,

$$N_2 + O_2 \rightarrow 2NO \qquad (1)$$

which is prohibited in an ordinary reaction environment, proceeds efficiently in a rare-gas cluster (size of 125) containing $N_2$ and $O_2$, when the cluster is impacted on a solid surface.[3−7] The efficiency of the four-center reaction is proved to be much higher in a larger cluster. Experimentally, Even and co-workers have shown that a four-center-like reaction,

$$(CH_3I)_n^- \rightarrow I_2^- \qquad (2)$$

takes place when a $CH_3I$ cluster anion, $(CH_3I)_n^-$, is impacted on a diamond-coated silicon surface.[31] On the other hand, Märk and co-workers have studied a cluster-impact reaction of acetone cluster cations on a stainless-steel plate, and found a kind of proton-transfer.[43]

A cluster-impact reaction in a small cluster provides a suitable basis to obtain a general feature of size-dependent cluster-impact reactions through generalizing the picture that we obtain in such a small cluster system. In this connection, we investigated a cluster-impact reaction of a carbon disulfide cluster anion, $(CS_2)_n^-$, onto Si(111) and $(La_{0.7}Ce_{0.3})B_6(100)$ surfaces. The carbon disulfide cluster anion was employed, because a sulfur atom in the cluster anion has (1) several oxidation numbers, which facilitate easy rearrangement of chemical bonds, and possesses (2) a relatively large electron affinity, so that a probability of charge neutralization is expected to be suppressed when the cluster anion interacts with a solid surface. In addition to these benefits, intensive investigations have been made on the geometric and electronic structures of this cluster anion. For instance, the photoelectron spectra[44] of $(CS_2)_n^-$ show that the dimer anion ($n = 2$) has the two isomers, $CS_2^-(CS_2)$ and $C_2S_4^-$, while all the other cluster anions consist of one monomer core ion. Actually, two different reaction channels have been recognized in the photodissociation of the dimer anion: one through its monomer core and the other through its dimer core.[45,46] Comparison of the results on these two cluster systems enables us to clarify how the structure of the core ion affects the cluster-impact reaction. A further benefit of employing carbon disulfide is that it has a chemical analogue, $(OCS)_n^-$, which has similar chemical properties and its photodissociation study has been undertaken as well.[47]

It is unavoidable to conduct the measurement at low collision energies if one would elucidate the mechanism of a cluster-impact reaction. In such a measurement, an impinging anion tends to be neutralized and hence the intensities of the product anions are significantly low. To avoid the neutralization, it is essentially necessary to use a solid surface with the smallest possible work function in an experimental point of view. It has been shown that the ion-surviving yield after a surface impact depends on the work function of the surface and the electron affinity of a chemical species of interest. To this end, a

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10.1021/jp012556u CCC: $22.00

$(La_{0.7}Ce_{0.3})B_6(100)$ having the work function of 2.52 eV was employed as a sample surface on which slow collision measurements will be performed.

## Experimental Section

Only a brief description related to the present study is shown in this paper, because the experimental details have been reported elsewhere.[34,38] The measurement was performed in a tandem time-of-flight (TOF) mass spectrometer equipped with a cluster ion source and a collision chamber in which a parent cluster anion is allowed to collide onto a target surface. A liquid sample of $CS_2$ (Kanto Chemical Co. Ltd., more than 99% pure) was placed in a stainless-steel vessel at room temperature. Vapor of $CS_2$ was introduced into a stainless cylinder in order to prepare a ~3:7 mixture of $CS_2$ and helium gas (Nippon Sanso, more than 99.9999% pure). The gas mixture was expanded into vacuum at a stagnation pressure of ~1.2 atm through a pulsed nozzle (General Valve, series No.9) having a repetition rate of 10 Hz. Clusters through the nozzle were ionized by impact of electrons having an energy of ~200 eV and a current of ~300 $\mu$A. In the $(OCS)_n^-$ preparation, pure OCS gas (Takachiho, 96% pure) was expanded at a stagnation pressure of 1.5 atm. Cluster anions thus produced were introduced into the acceleration region of the primary TOF mass spectrometer through a skimmer with a hole of 2 mm diameter. A cluster anion with a given size was selected out by a mass gate placed in the primary TOF mass spectrometer, and was allowed to collide onto a surface placed at the bottom of a reflectron at an ambient pressure of $2 \times 10^{-8}$ Pa. Anions scattered from the surface were accelerated in the reflectron, and detected by a tandem microsphere-plate (MSP, El-Mul E033DTA with an effective diameter of ~32 mm) placed in the secondary TOF mass spectrometer. The intensities of the product anions from a given parent cluster anion were obtained by accumulating the signal for 60 s in a storage oscilloscope (Tektronix TDS-520). The statistical errors in the intensities of the product anions were found to be 10% of the anion intensities. The collision energy per core ion ($CS_2^-$), $E_{col}$, was varied from 50 to 3000 eV by changing the bias voltage applied to the silicon surface. A smaller bias voltage (0−300 V) was applied to the $(La_{0.7}Ce_{0.3})B_6$ surface so that the collision energy was much less. The collision measurement was performed by setting the beam axis of an incident cluster anion at 2° with respect to the direction normal to the sample surface.

The silicon surface was prepared from a p-type doped Si(111) wafer ($25 \times 15$ mm$^2$, specific resistance of 1−10 Ω cm), and was cleaned by resistive heating with the aid of electron bombardment as follows: (1) the surface is baked at 800 °C overnight, (2) flashed at 1050 °C for 10 s with keeping the pressure of the chamber at less than $4.5 \times 10^{-8}$ Pa, (3) cooled quickly to 800 °C and slowly to room temperature at a rate of 3 °C per second. Each measurement was completed within 30 min after the surface treatment. A $(La_{0.7}Ce_{0.3})B_6(100)$ surface was also employed as a sample surface. A $(La_{0.7}Ce_{0.3})B_6(100)$ sample crystalline was prepared by the floating zone method.[48] The surface ($20 \times 9$ mm$^2$) was installed on a holder made of graphite, and cleaned by heating at ~1300 °C for 1 min by means of electron bombardment.

## Results

**Impact of $(CS_2)_n^-$ on a Si(111) Surface.** The scattered anions are $S_m^-$ ($m = 1-3$) in addition to a trace amount of $Si_m^-$ ($m = 1-2$). In the entire collision energy range studied (50−300 eV), the product anions were found to be $S^-$ from $(CS_2)_n^-$ ($n \geq 1$), $S_2^-$ from $(CS_2)_n^-$ ($n \geq 2$), and $S_3^-$ from $(CS_2)_n^-$ ($n \geq 5$). As described later, $S^-$ is produced by dissociation of the core ion, $CS_2^-$, in $(CS_2)_n^-$, while $S_2^-$ and $S_3^-$ by an intracluster reaction.

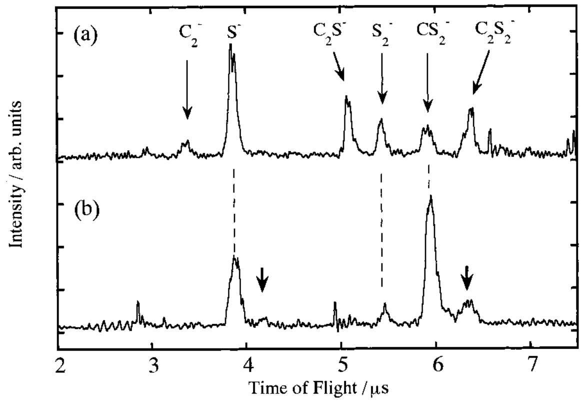

**Figure 1.** Mass spectra of anionic species, $C_2^-$, $S^-$, $C_2S^-$, $S_2^-$, $CS_2^-$, and $C_2S_2^-$, produced by impacts of $(CS_2)_2^-$ (see panel (a)) and of $(CS_2)_3^-$ (panel (b)) at the collision energy per $CS_2$ of 50 eV. In panel (a), the parent anion, $(CS_2)_2^-$, is isotopically pure for sulfur, so that no isotopic complexity exists in the spectrum. In panel (b), on the other hand, the parent anion, $(CS_2)_3^-$, contains isotopic species. In fact, the isotopic species are discernible in the mass spectrum of the product anions (indicated by arrows).

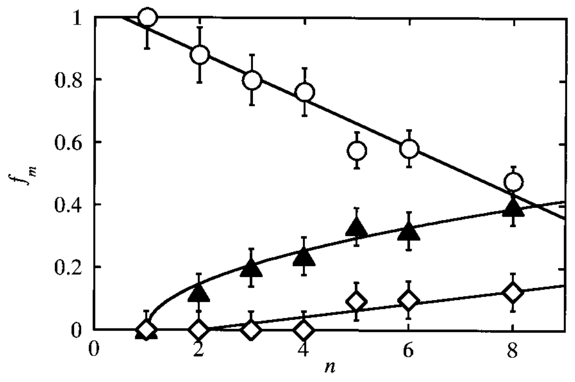

**Figure 2.** Branching-fraction, $f_1$(○), $f_2$(▲), and $f_3$(◇), for the production of $S^-$, $S_2^-$, and $S_3^-$, respectively, plotted against the cluster size, $n$, in the impact of $(CS_2)_n^-$ at the collision energy (per $CS_2$) of 100 eV. The solid curves show eye guides. See text for the definition of $f_m$ ($m$ = 1−3).

**Impact of $(CS_2)_n^-$ on a $(La_{0.7}Ce_{0.3})B_6(100)$ Surface.** Figure 1 shows typical mass spectra of anions produced by the impact of $(CS_2)_2^-$ and $(CS_2)_3^-$ on a $(La_{0.7}Ce_{0.3})B_6$ surface at the collision energy of $E_{col} = 50$ eV. Anions, $S^-$, $C_2S^-$, $S_2^-$, $CS_2^-$, and $C_2S_2^-$, are produced from $(CS_2)_2^-$, while $S^-$, $S_2^-$, and $CS_2^-$ are produced from $(CS_2)_3^-$. The hydrogen anion may originate from contaminants on the surface because neither the incident cluster nor the surface contain any hydrogen atoms. The ion surviving yield in the impact of $(CS_2)_2^-$ on a $(La_{0.7}Ce_{0.3})B_6(100)$ at $E_{col} = 100$ eV was ~0.6% while that on a Si(111) surface was ~0.01%, where the yield is defined by the ratio between the total intensity of all the product anions and the intensity of the parent cluster anion.

**Branching Fractions of Product Anions.** Figure 2 shows branching fractions, $f_m$,

$$f_m = \frac{[S_m^-]}{\sum_m [S_m^-]} \quad (m = 1-3), \tag{3}$$

as a function of the cluster size, $n$, at $E_{col} = 100$ eV, where [A]

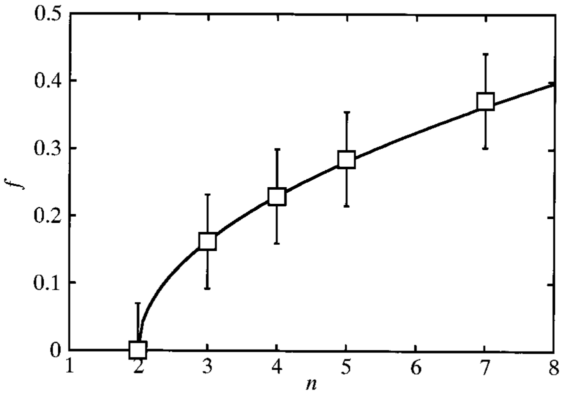

**Figure 3.** Branching-fraction, $f_2$, for the production of $S_2^-$ plotted against the cluster size, $n$, in the $(OCS)_n^-$ impact at the collision energy (per OCS) of 100 eV. The solid curve shows an eye guide. See text for the definition of $f_2$.

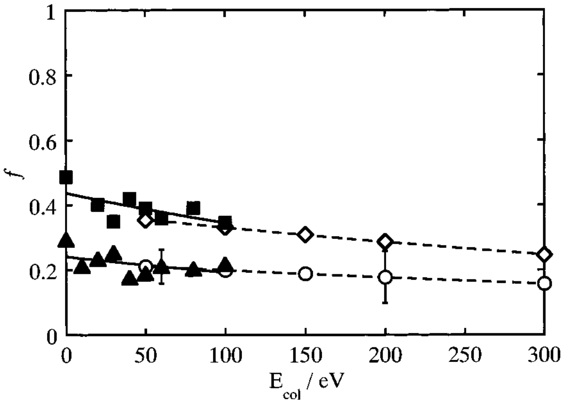

**Figure 4.** Collision-energy dependence of the branching-fraction, $f_2$, for the production of $S_2^-$ in the $(CS_2)_3^-$ and $(CS_2)_5^-$ impacts on a $(La_{0.7}Ce_{0.3})B_6$ surface(▲,■) and a Si(111) surface (○,◇), respectively. The solid and dotted curves show eye guides. See text for the definition of $f_2$.

represents the intensity of species A. As shown in Figure 2, $f_2$ and $f_3$ increase with $n$. Note that $f_3$ is very small in the $n = 1-4$ range.

In the $(OCS)_n^-$ impact, $S^-$ and $S_2^-$ were dominant product anions; $S^-$ was always produced but $S_2^-$ was produced only from $(OCS)_n^-$ ($n \geq 3$). Figure 3 shows $f_2$ plotted against $n$ at $E_{col} = 100$ eV, where the definition of $f_2$ is same as eq 3. As shown in Figure 3, $f_2$ increases with $n$.

## Discussion

**Cluster-Impact Reaction on Two Different Surfaces.** As described in the Introduction, the intensity of a product anion scattered from the silicon surface is reduced due to charge neutralization when the collision energy is lowered. To minimize the neutralization, the low energy measurement was performed on a $(La_{0.7}Ce_{0.3})B_6$ surface having a much smaller work function. It was found that essentially the identical reaction proceeds on the two different surfaces, as described below. We paid attention to the two product anions, $S^-$ and $S_2^-$, because these are main products observed commonly on the two surfaces. The branching fraction, $f_2$, was employed as a propensity for the comparison. Figure 4 shows the collision-energy dependence of $f_2$ for the $(CS_2)_3^-$ and $(CS_2)_5^-$ impacts on the silicon and the $(La_{0.7}Ce_{0.3})B_6$ surfaces. In cluster sizes more than 2, the $f_2$ values for the two surfaces agree in the energy range of 50−100 eV where the branching fraction was measured on both the surfaces. It implies that essentially the same reaction mechanism for the $S_2^-$ production operates on the two surfaces except for $n = 2$.

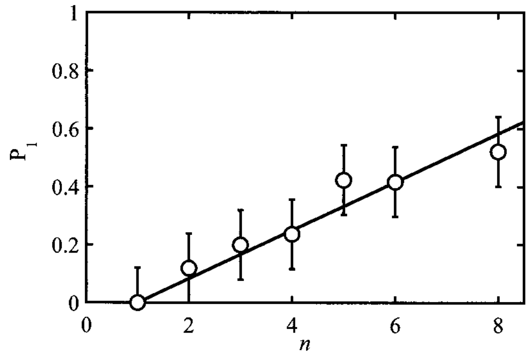

**Figure 5.** Probabilities, $P_1$, for S abstraction by $S^-$, plotted against the cluster size, $n$. The solid curve shows an eye guide. See text for the definition of $P_1$.

**Reaction Scheme.** Bierbaum and co-workers have shown that in the collision of $S^-$ with $CS_2$ in the gas phase, a sulfur-abstraction reaction

$$S^- + CS_2 \rightarrow S_2^- + CS \tag{4}$$

proceeds most efficiently with an activation energy of 0.7 eV,[49] and $S_3^-$ is successively produced by further sulfur abstraction by $S_2^-$ from $CS_2$,

$$S_2^- + CS_2 \rightarrow S_3^- + CS \tag{5}$$

Reactions 4 and 5 proceed also in the cluster−surface impact. Formation of $S_2^-$ due to unimolecular dissociation of $CS_2^-$ is ruled out because no $S_2^-$ is produced by impact of $CS_2^-$ onto the surfaces of Si and $(La_{0.7}Ce_{0.3})B_6$. Formation of $S_2^-$ by a four-center reaction between $CS_2^-$ and $CS_2$ is highly unlikely because of its low reaction cross section even in the surface-impact.[11]

As argued in the previous section, both the surfaces employed in the present experiment give almost identical results as far as the reaction scheme considered in the present study is concerned.

**Comparison between Cluster-Impact Reaction and Gas-Phase Reaction.** The probability, $P_1(n)$, of the sulfur abstraction by $S^-$ in one event of the cluster impact is expressed in terms of the branching fractions, $f_m$, as

$$P_1(n) = f_2(n) + f_3(n) \tag{6}$$

where $n$ represents the cluster size. In the collision of $(CS_2)_n^-$, the number of $CS_2$ molecules is $n - 1$, and hence $P_1(n)$ is proportional to $(n - 1)$, or

$$P_1(n) = \alpha_1(n - 1) \tag{7}$$

where $\alpha$ represents a probability of the sulfur abstraction by $S^-$ in collision with one $CS_2$. Fitting of the $n$-dependence of $P_1(n)$ with eq 7 gives $\alpha_1 = 0.08 \pm 0.03$ (See Figure 5).

Comparing these results with those obtained for the gas-phase reaction, one obtains a number of collisions between molecules in the cluster impact. The probability, $\alpha_g$, of the sulfur abstraction per single collision in the gas phase is expressed in terms of its rate, $v$, and the collision frequency, $z$, as

$$\alpha_g = v / z \tag{8}$$

The rate, $v$, is calculated by using the rate constant reported by Bierbaum and co-workers.[49] To calculate $z$, we employed the Langevin cross section as the collisional cross section, because $S^-$ and $CS_2$ are attracted by a charge-induced dipole

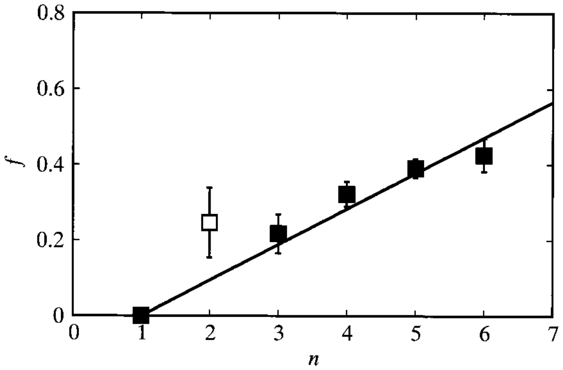

**Figure 6.** Branching-fraction, $f_2$, for the production of $S_2^-$ in the $(CS_2)_n^-$ impact, at the collision energy (per molecule) of 50 eV. The solid curve shows an eye guide.

interaction. For the temperature estimation, we consulted with our previous experimental result that the effective temperature of the product anions in the silicon surface-impact of the cluster anion, $I_2^-(CO_2)_{1-30}$, is 6000−12000 K.[32] Similarly, it is assumed that the whole collision system reaches quasi-equilibrium with an effective temperature of 10 000 K. By inserting all the necessary values in eq 8, $\alpha_g$ is obtained to be $0.09 \pm 0.01$. The uncertainty in $\alpha_g$ originates mainly from that (±5000 K) in the temperature. The number of collision between the molecules in the cluster impact is obtained to be ~1. Let us consider a case that a product $S^-$ from the surface is scattered back to the surface in collision with a solvent $CS_2$ molecule and is bounced back again toward the same solvent $CS_2$ molecule. The probability of this case occurring is estimated to be less than 10% by using the Langevin cross section of $S^-$ with $CS_2$. This probability turns out to be the highest possible probability that $S^-$ collides with the same solvent molecule twice.

**Surface-Impact Reaction of Dimer.** In the impact of a $CS_2$ dimer anion, $C_2S_2^-$ is observed as a product anion in addition to $S^-$ and $S_2^-$ (see Figure 3). It is likely that $C_2S_2^-$ is produced from an isomer present in the parent dimer ion. This conjecture is consistent with the deviation of the $f_2$ value (see eq 3 for definition) in the linear relation of $f_2$ against $n$ (see Figure 6) as argued below.

It has been reported that a $CS_2$ dimer anion has two isomers: one has a monomer core ion, $CS_2^-(CS_2)$, and the other is a molecular ion, $C_2S_4^-$.[44,45,50] Photodissociation of $(CS_2)_n^-$ has shown that a cluster ion with a $C_2S_4^-$ core ion produces $C_2S_2^-$ while a cluster ion with a $CS_2^-$ core ion does not.[46] These results suggest that $C_2S_2^-$ is produced by surface-impact dissociation of $C_2S_4^-$. As shown in Figure 6, the $f_2$ value incleases linearly with the cluster size, $n$, except for the dimer ion ($n = 2$); the $f_2$ values deviate upward from the linear relationship at $n = 2$. By considering that $(CS_2)_n$ with $n \geq 3$ has a monomer core such as $CS_2^-(CS_2)_{n-1}$, the upward deviation in the $f_2 - n$ relation at $n = 2$ implies that $S_2^-$ is produced from both $CS_2^-(CS_2)$, and $C_2S_4^-$, and the efficiency for the $S_2^-$ production from $C_2S_4^-$ is larger than that from $CS_2^-(CS_2)$.

**Reactions of $(OCS)_n^-$.** In the $(OCS)_n^-$ impact, the branching fraction, $f_2$, for the $S_2^-$ increases with the cluster size, $n$, in a manner similar to that observed in the $(CS_2)_n^-$ impact (see Figures 4 and 5). On this analogy, the following sulfur-abstraction reaction proceeds in the impact of $(OCS)_n^-$: $S^-$ is produced by surface-impact dissociation of the core ion, $(OCS)_2^-$,

$$(OCS)_2^- \rightarrow S^- \qquad (9)$$

and the $S^-$ thus produced successively abstracts an sulfur atom from a solvent OCS by intracluster collision,

$$S^- + OCS \rightarrow S_2^- + CO \qquad (10)$$

## Conclusions

We have studied an intracluster reaction of size-selected $(CS_2)_n^-$ and $(OCS)_n^-$ induced by impact on two surfaces, Si(111) and $(La_{0.7}Ce_{0.3})B_6$, which possess larger and smaller work functions, respectively. The reaction proceeds in such a manner that $S^-$ produced from core−ion dissociation preludes its sulfur abstraction from an adjacent solvent molecule. Essentially the same reaction mechanism operates on the both surfaces. Charge neutralization is more greatly suppressed by using a surface having a lower work function.

**Acknowledgment.** The authors are sincerely grateful to Professor T. Nagata (University of Tokyo) and Professor T. Tsukuda (Institute of Molecular Science) for information on photodissociation of $(CS_2)_n^-$. Dr. H. Okano, Dr. N. Hayasaka, and Dr. M. Nagamine (Research and Deportment Center, Toshiba Corp.) are also acknowledged greatly for supplying silicon wafers used in the present study and their advice on the surface preparation. This research was supported by the Special Cluster Research Project of Genesis Research Institute, Inc.

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